Supplementary Information

Sorption of Imidacloprid and Hexazinone to Polyethylene Microplastics

Karen N. Morishita,[a,b] Mariana A. Dias,[a] Camila L. Madeira,[a,c] and Cassiana C. Montagner*[*,a]

[a]Departamento de Química Analítica, Instituto de Química, Universidade Estadual de Campinas (UNICAMP), 13083-970 Campinas-SP, Brazil

[b]Department of Chemical and Environmental Engineering, College of Engineering and Applied Sciences, University of Cincinnati, 45221 Cincinnati-OH, United States

[c]Department of Civil, Environmental and Construction Engineering, Miguel A. Loya College of Engineering, University of Texas, 79968 El Paso-TX, United States

*e-mail: ccmonta@unicamp.br

Editor handled this article: Josué Carinhanha Caldas Santos (Associate)

Karen Noda Morishita: https://orcid.org/0000-0002-1951-7996

Mariana Amaral Dias: https://orcid.org/0000-0003-0639-5288

Camila Leite Madeira : https://orcid.org/0000-0001-9872-9868

Cassiana C. Montagner: https://orcid.org/0000-0002-6475-5969

Analytical and sorption method validation

Method validation was performed by the assessment of the following figures of merit: selectivity, limit of detection, limit of quantification, linearity, accuracy, within-run precision, solution stability, and filter assessment.

Selectivity

During the sorption experiments, negative controls chromatograms were compared to sample chromatograms to attest no matrix interferences were present at the analyte retention time (Figure S1). Besides, the peak purity of both analytes in all matrices was assessed using LabSolutions LCsolution version 1.21 SP1© 2002-2005 (Shimadzu Corporation, Kyoto, Japan) (Figure S2). The parameters used for this assessment were wavelength range of 210 to 400 nm in a 1-minute range from the chromatogram with little interference.

Limit of detection

The limit of detection was defined as 3 μg L^{-1} for both imidacloprid and hexazinone in which the signal-to-noise ratio was at least 3.

Limit of quantification

The limit of quantification was defined as 5 μg L^{-1} for both imidacloprid and hexazinone in which the concentration in which the signal-to-noise ratio was at least 10.

Linearity

An analytical curve containing both analytes was prepared in triplicate at the concentrations: 5, 25, 50, 100, 150 and 200 μg L^{-1}. Each solution was injected three times.

Each concentration level was tested for the presence of outliers by applying Grubbs' test at 95% level of confidence (Figure S3) as for all the other statistical tests in this study. All calculated G values were smaller than the G critical value, therefore no point was considered an outlier. Next, the homogeneity of variance between levels was assessed using Cochran's test. Both models were considered homoscedastic as calculated C values were smaller than the C critical value.

The linear model was calculated using the ordinary minimum squares method, and the correlation was evaluated using the determination coefficient r^2 (Figure S4 and Table S2). Standardized residuals lower or equal to –2 and higher or equal to +2 were evaluated as possible outliers using Cook's squared distance (CD^2). Both CD^2 evaluated values were smaller than 1, and therefore were not omitted from the data set.

Finally, the significance of regression was evaluated using Analysis of Variance (ANOVA). The calculated F values were higher than the F critical value. Therefore, the regression was considered significant.

Accuracy

Each one of the types of matrices was homogenized for approximately 5 days with microplastics, then filtered with cellulose acetate membrane of pore size of 0.45 μm, spiked in triplicate with both analytes at the concentrations 5, 25, 50, 100, 150, and 200 μg L^{-1} and injected in triplicate. Recoveries are presented in Figure S5.

Within-run precision

Variation coefficients for each one of the levels for each one of the matrices was calculated to assess the precision. All values are smaller than the values presented by AOAC guidelines,[1] with exception of recovery obtained for hexazinone at 5 μg L^{-1} level which variation coefficient was 45%.

Stability of solution

Stability of solution was evaluated by: (*i*) reinjections of calibration solutions; (*ii*) re-dilutions of work solution in ultrapure water; (*iii*) positive controls in each sorption experiment. These results are presented in Figures S6 and S7.

Filter assessment

Areas of both analytes in the solution without filtration were compared to areas of solution filtered with polyvinylidene fluoride (PVDF) syringe filter of pore size of 0.22 μm and 13 mm of diameter (Figure S8). A *t*-test was performed to determine if there was difference between areas.

Sorbents characterization

Infrared spectra for PE MP [polyethylene (PE); microplastics (MP)] (Figure S14) obtained in an ATR-FTIR (Cary 630, Agilent, Santa Clara, U.S.) were compared with Open Specy library for confirmation of the identity of the polymer, generating a Person's r of 0.97 with a PE spectra from the database.[2]

A SEM-EDS analysis was conducted using a scanning electron microscope Quanta 250 (FEI Company, Hillsboro, U.S.) and an energy dispersive X-ray spectroscope X-Max50 (Oxford Instruments, Abingdon, England). The elemental composition was 99.5 ± 0.3% of carbon and 0.5 ± 0.3% of oxygen. Images obtained in this analysis are presented in Figure S13.

Surface area was determined using the physical adsorption technique using a Nova 4200e instrument (Quantachrome, Graz, Austria) by the BET method in the software Quantachrome NovaWin version 10.01. PE MP surface area was 21.4 m^2 g^{-1} and sand surface area was 1.7 m^2 g^{-1}.

The particle size distribution was determined using a binocular optical microscope (Quimis, Diadema, Brazil) coupled to an Infinity 1 TV Lens C-0.6x camera (Nikon, Minato, Japan). Particles were dispersed on a glass slide, and pictures (Figure S12) were shot along the glass slide length using the software Image-Pro Plus (Media Cybernetics, Silver Spring, U.S.). To set the scale, a calibration slide with 1 mm *per* 100 division was used. Using the software Fiji Image J,[3] the length of at least 300 particles was measured. The particle size distribution of PE MP and sand is presented in Figure S14. The average particle length for PE MP was 83 μm (n = 316) and for sand was 228 μm (n = 300).

Exploratory sorption efficiencies of imidacloprid and hexazinone to different sorbents

The interaction of imidacloprid and hexazinone to different sorbents was evaluated. Rotation of the roto-torque agitator was kept at 40 rpm, and the initial concentration of each one of the analytes in ultrapure water was 50 μg L^{-1}. The sorbents included:

Polystyrene (PS): PS pellets (Aldrich Chemical Company Inc., Milwaukee, U.S.) of average molecular weight of 280,000 were submerged in liquid nitrogen then ground and sieved in sieves (Bertel, Caieiras, Brazil) of pore size of 500 µm and 106 µm.

Degraded polystyrene (PSd): PS obtained after sieving using a 500-µm pore size sieve and retained in the 106-µm pore size sieve was degraded for 188 h in a UV-C chamber.

Polyethylene (PE): PE described in the manuscript. According to the Certificate of Analysis, its melting point is 134 °C, which classifies it as a high-density polyethylene. No information about the additives in the product formulation was made available by the manufacturer.

Polyamide (PA): polyamide pellets (Nylon 6 – Domamid H24; DOMO Chemicals, Ghent, Belgium) were submerged in liquid nitrogen then ground and sieved in sieves (Bertel, Caieiras, Brazil) of pore size of 500 and 106 µm.

Polyethylene terephthalate (PET): PET pellets (Rhodia-ster) were submerged in liquid nitrogen then ground and sieved in sieves (Bertel, Caieiras, Brazil) of pore size of 500 and 106 µm.

Polymethyl methacrylate (PMMA): PMMA was grounded using a mortar and pestle.

Polyvinyl chloride (PVC): PVC powder was used as it was.

Activated carbon: activated carbon (Synth, Diadema, Brazil) was used as it was.

Sand: sand described in the manuscript.

Soil: clay soil (70% clay; 16% silt; 14% sand) with 3.98% (m/v) or organic matter.

Dilution effect quality controls

Apart from the samples prepared in triplicate for each matrix tested, 5 controls were also evaluated in this study.

Sorption control: These test tubes were prepared exactly like the samples, but no second solution was added.

Stability control: These test tubes were prepared exactly like the samples, but no PE MP nor second solution was added.

Dilution control: These test tubes were prepared exactly like the samples, but no PE MP was added.

Negative control: These test tubes contained only ultrapure water and PE MP. No second solution was added.

Negative dilution control: These test tubes contained only ultrapure water. The same second solution used for the sample was added.

Table S1. Geographic coordinates of sampling sites

Sampling site	Geographic coordinate
Source of Pedras Creek	22°51'45.1"S 47°03'24.1"W
Pedras Creek	22°49'33.2"S 47°04'30.0"W
Anhumas Creek	22°45'56.8"S 47°06'02.4"W
Juquehy Beach	23°46'10.7"S 45°43'35.2"W

Table S2. Linearity equation and determination coefficients (r^2) for imidacloprid and hexazinone analytical method

	Imidacloprid	Hexazinone
Model equation	y = 532x + 750	y = 398x + 619
r^2	0.9988	0.9942

Table S3. Aqueous matrices characteristics used in kinetics study

	pH	TOC / (mg L^{-1})
Ultrapure water	8.4	0
Source of Pedras Creek	6.0	8.3
Pedras Creek	7.2	12.6
Anhumas Creek	7.5	14.5

TOC: total organic carbon.

Table S4. Metrics for comparison of kinetic models

	R^2	RSS	RMSE	χ^2
Imidacloprid				
Pseudo-first order	0.5282	0.8732	0.1678	0.02817
Pseudo-second order	0.5466	0.8393	0.1645	0.02707
Elovich	0.5609	0.8127	0.1619	0.02622
Hexazinone				
Pseudo-first order	0.5228	2.4978	0.2839	0.08058
Pseudo-second order	0.5377	2.4197	0.2794	0.07805
Elovich	0.5456	2.3787	0.2770	0.07673

R^2: determination coefficient, RSS: residual sum of squares, RMSE: root mean square error, χ^2: reduced chi-square.

Table S5. Metrics for comparison of isotherm models

	R^2	RSS	RMSE	χ^2
Imidacloprid				
Linear	0.8031	2.7447	0.3455	0.11934
Freundlich	0.3021	2.6364	0.3462	0.11984
Langmuir	–2.5662	13.4710	0.7825	0.61232
Hexazinone				
Linear	0.8743	4.1405	0.4243	0.18002
Freundlich	0.4426	3.5683	0.4027	0.16220
Langmuir	0.3946	3.8752	0.4197	0.17614

R^2: determination coefficient, RSS: residual sum of squares, RMSE: root mean square error, χ^2: reduced chi-square.

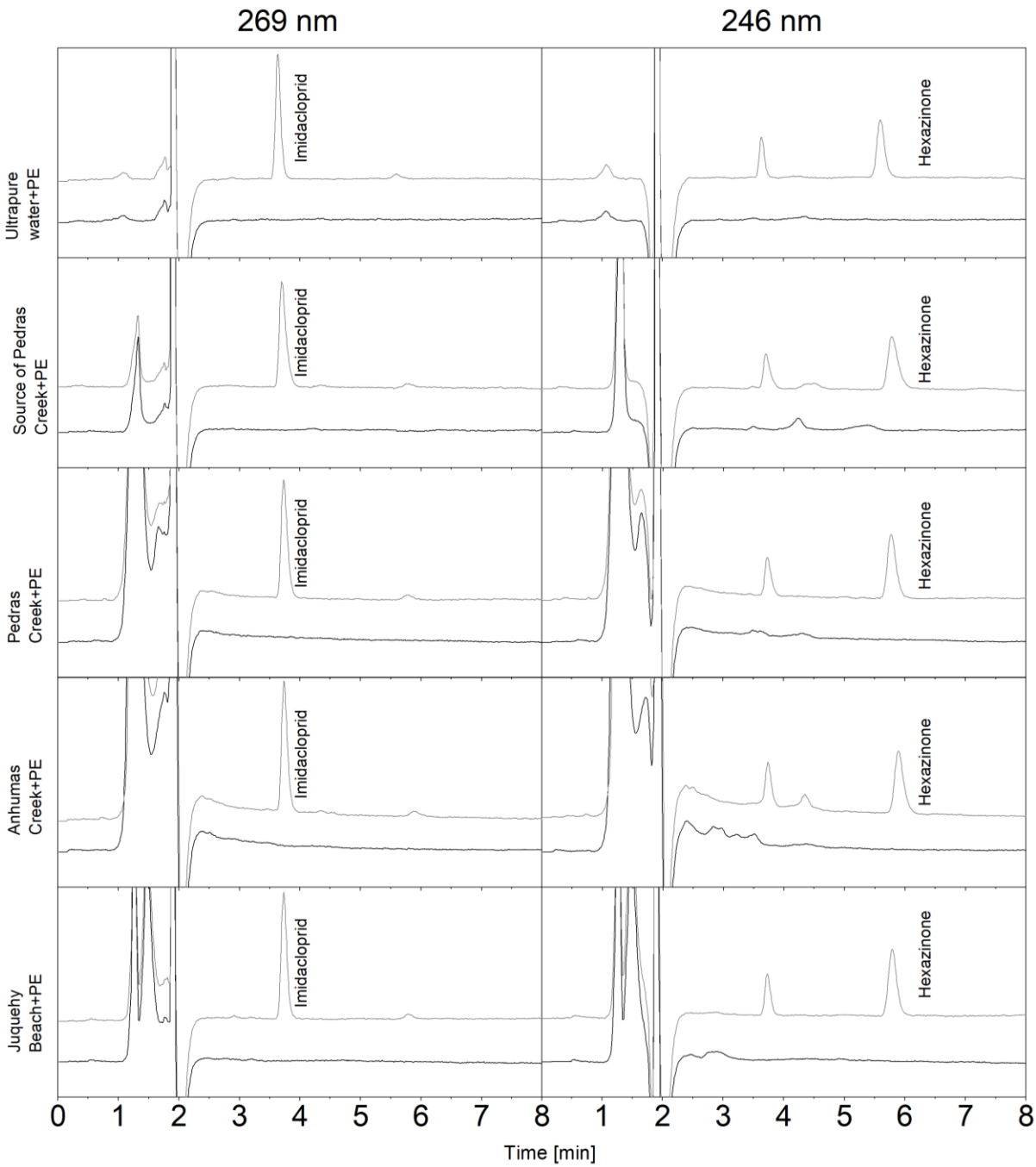

Figure S1. Matrices spiked with imidacloprid and hexazinone at 50 µg L^{-1} (gray chromatograms) and negative controls (black chromatograms).

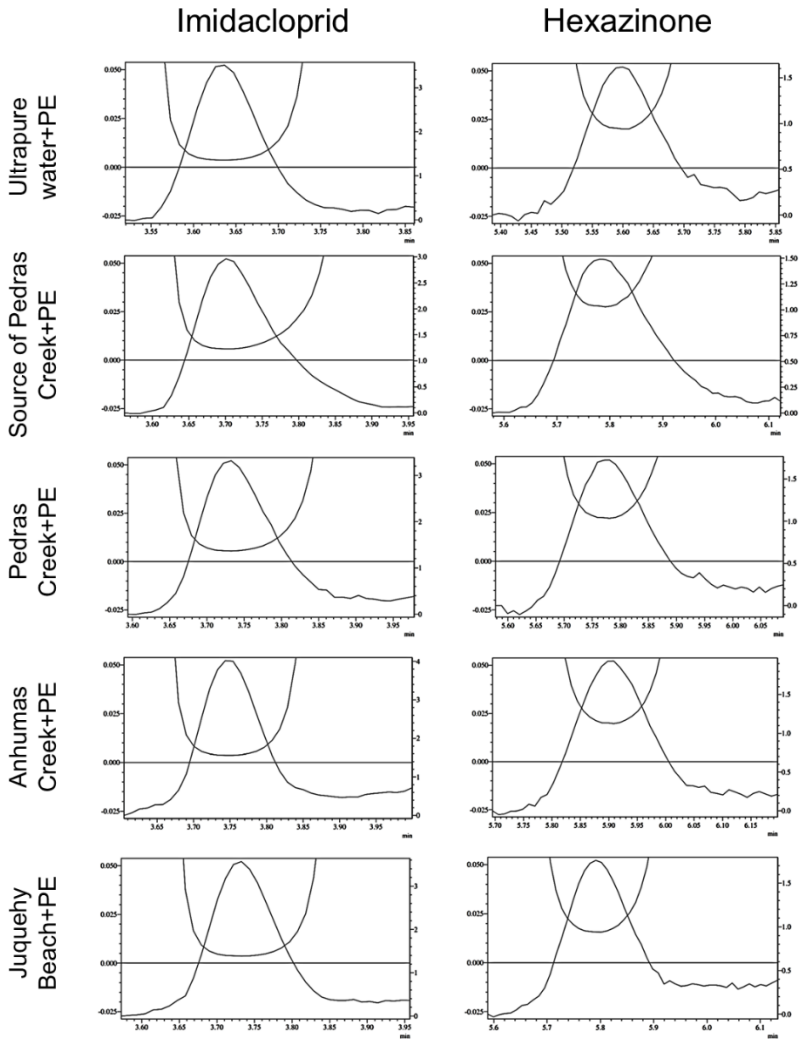

Figure S2. Graphic imidacloprid and hexazinone peak purity evaluation in different water matrices using LabSolutions software.

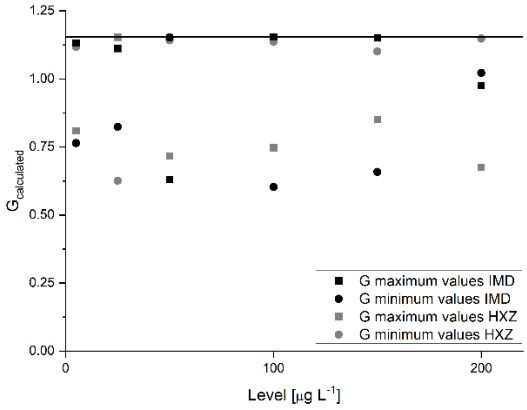

Figure S3. G values calculated on the Grubbs' test of imidacloprid (IMD) and hexazinone (HXZ) linearity data set.

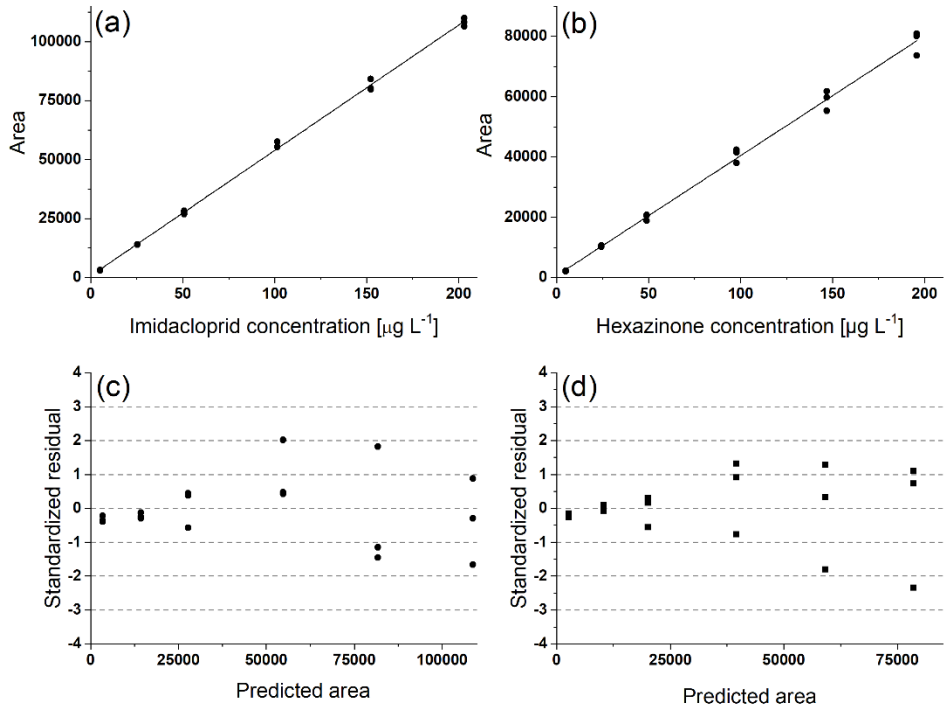

Figure S4. Linearity model for imidacloprid and hexazinone analytical method. (a) Analytical curve for imidacloprid; (b) analytical curve for hexazinone; (c) standardized residuals plot for imidacloprid linearity data; (d) standardized residuals plot for hexazinone linearity data.

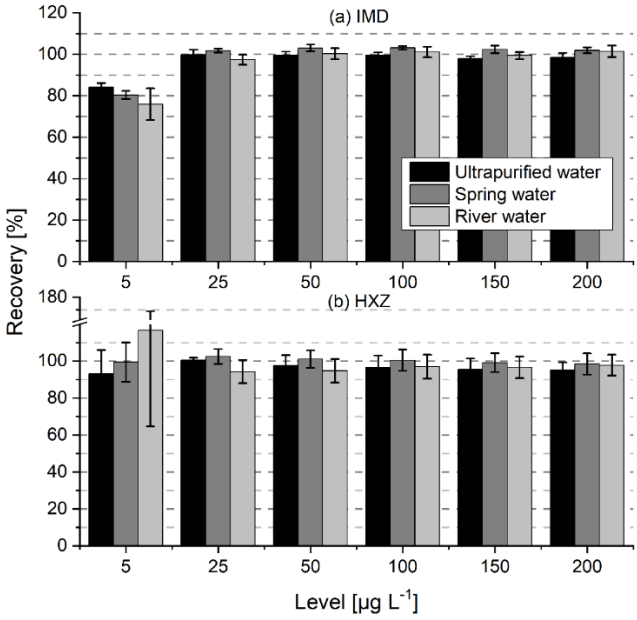

Figure S5. Imidacloprid (IMD) and hexazinone (HXZ) recoveries in accuracy test of analytical method.

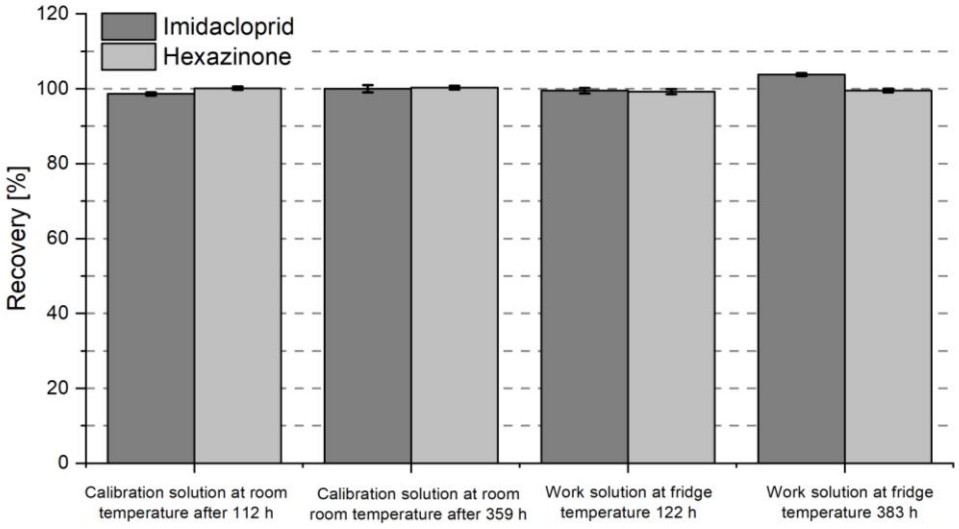

Figure S6. Standard solutions recoveries of imidacloprid and hexazinone.

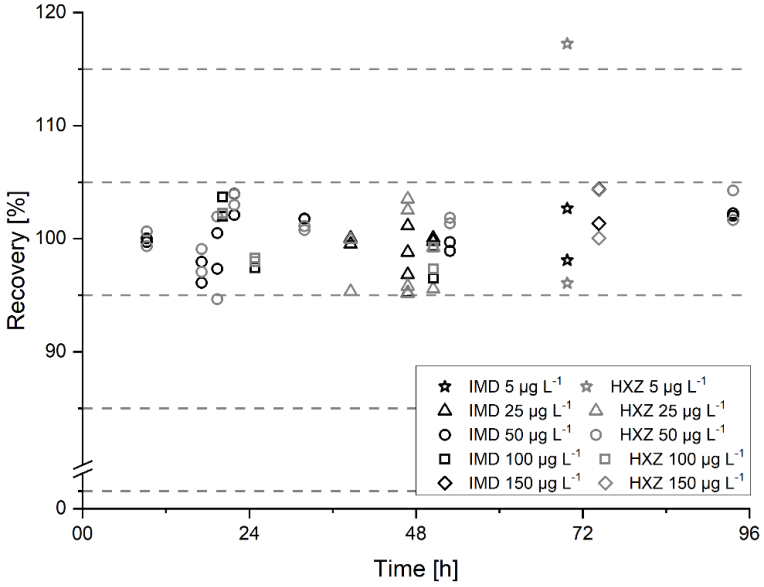

Figure S7. Quality control recoveries obtained during the list of injections of sorption studies.

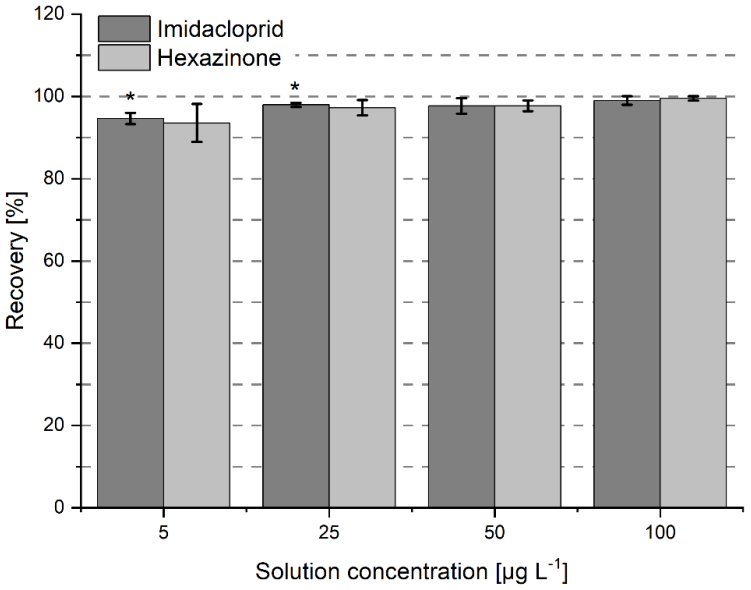

Figure S8. Imidacloprid and hexazinone recoveries in filtered solutions using PVDF syringe filter. The star indicates a significant difference to the expected value of 100%.

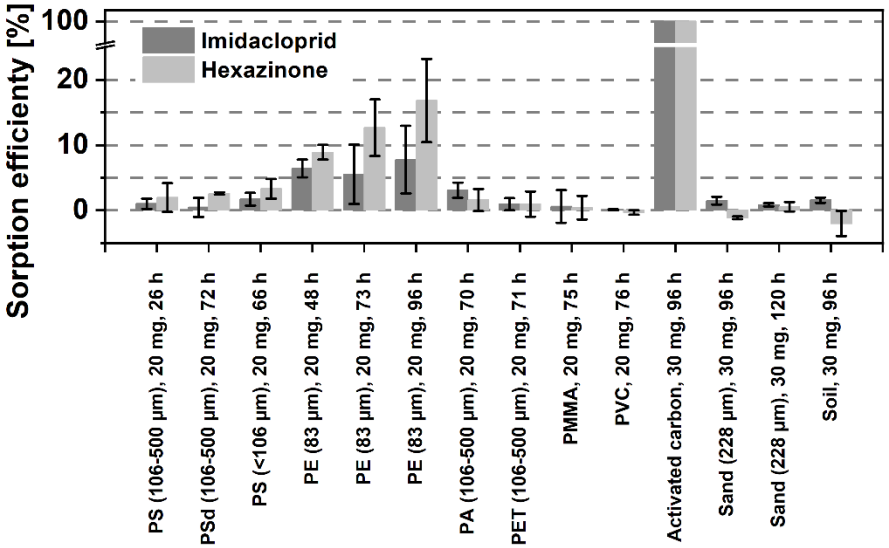

Figure S9. Exploratory sorption efficiencies of imidacloprid and hexazinone to different sorbents.

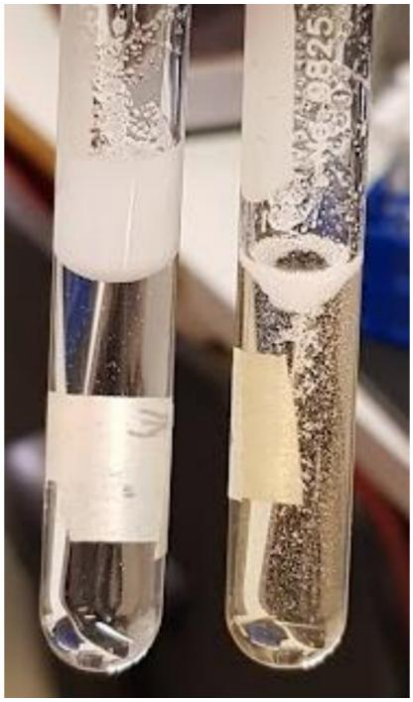

Figure S10. Test tubes immediately after shaking. On the left the solution contains ultrapure water and PE MP. On the right, the test tube contains ultrapure water, PE MP and humic acid.

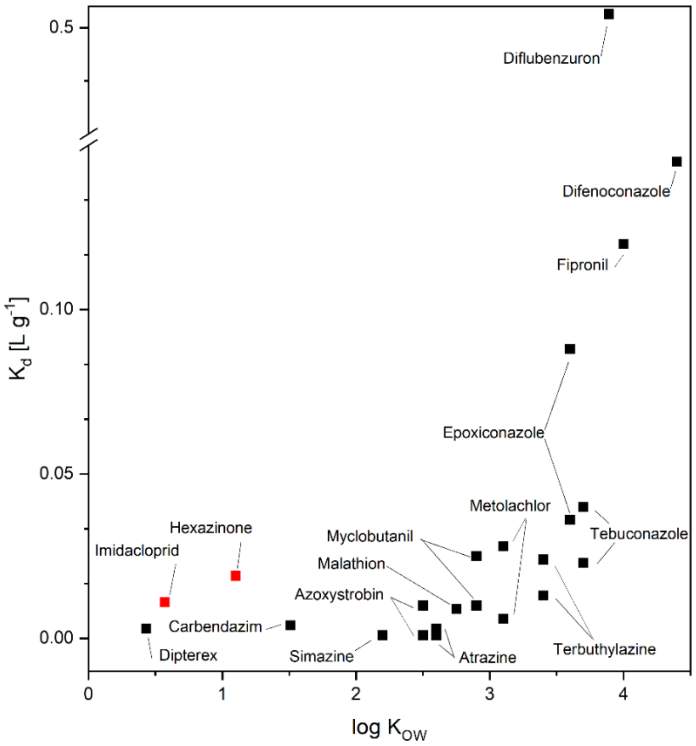

Figure S11. Pesticides sorption coefficients (K_d) to PE MP as a function of log K_{ow}. Red squares are the values obtained in this study, the other values were reported in literature.[4-6] Log K_{ow} that were not described in the respective references were obtained from PubChem database.

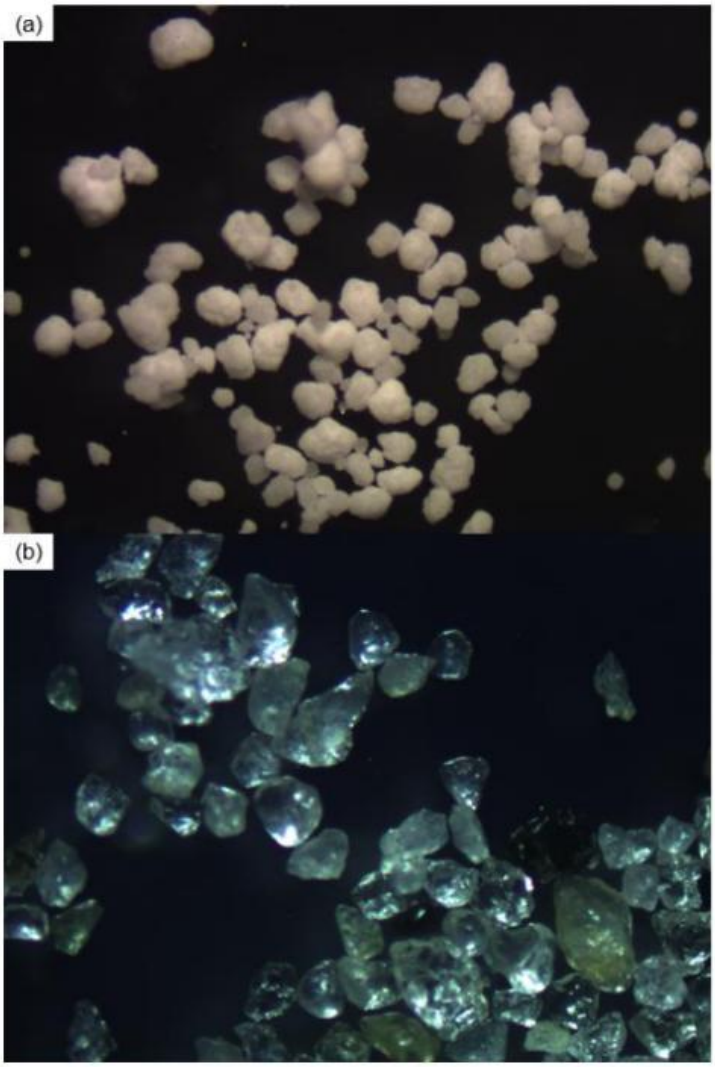

Figure S12. Optical microscopy of (a) PE MP and (b) sand at a magnification of 40×.

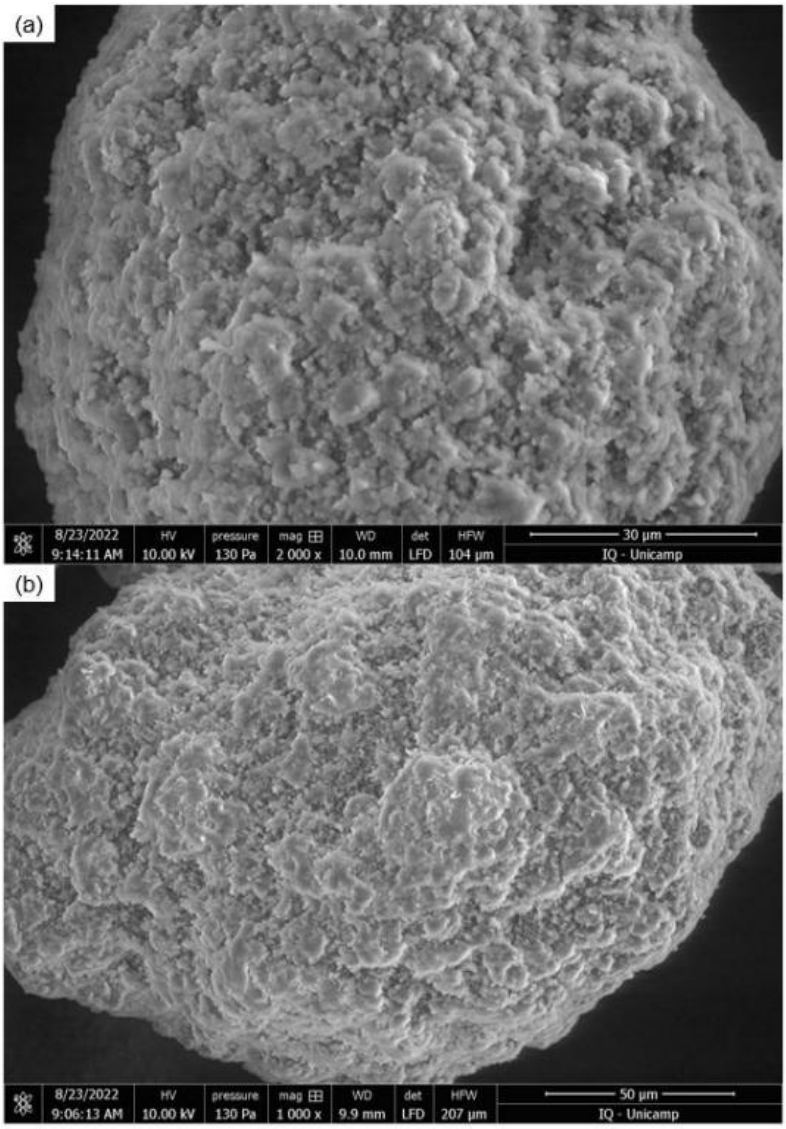

Figure S13. PE MP scanning electron microscopy at (a) 2000× and (b) 1000×.

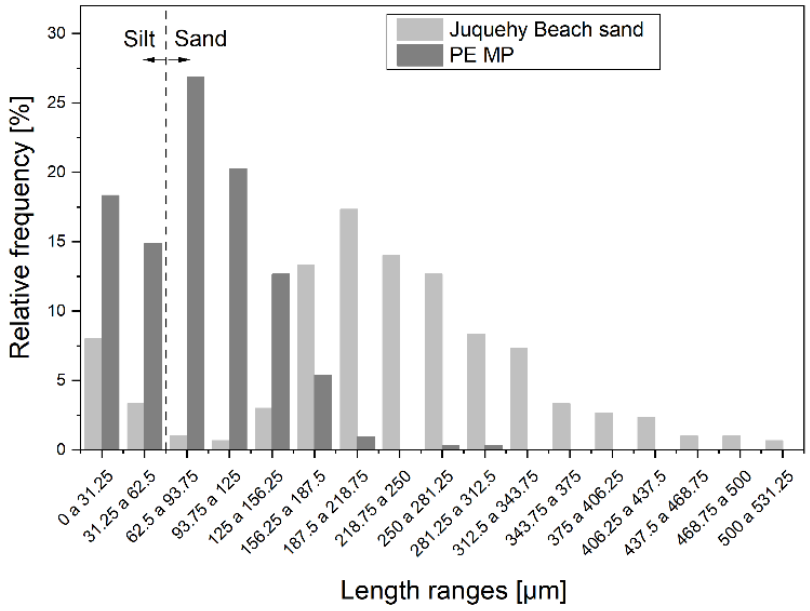

Figure S14. Particle size distribution.

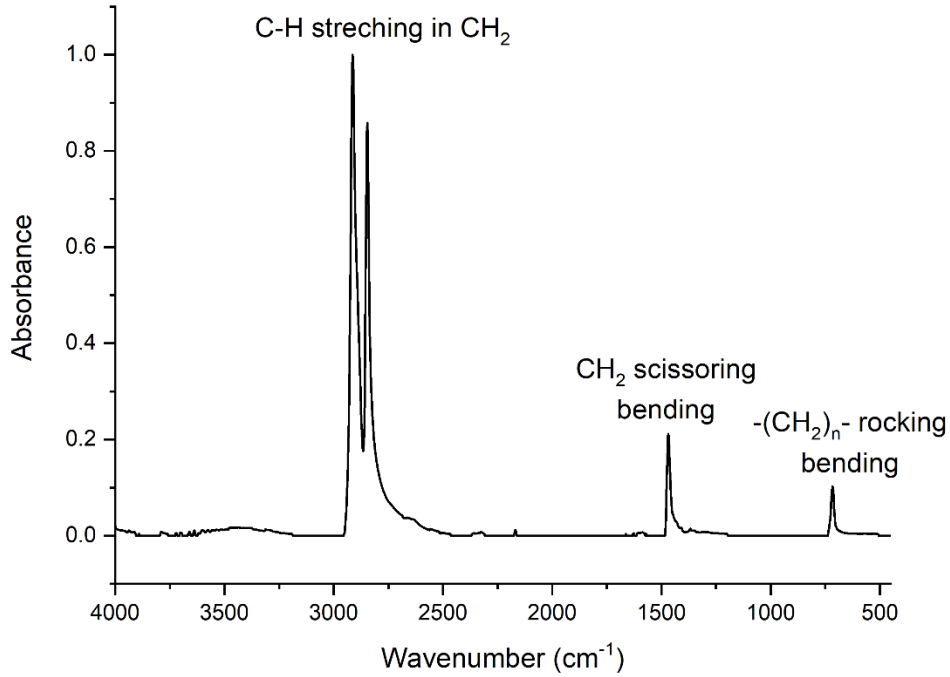

Figure S15. PE MP infrared spectra.

References

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